

TERMINAL STATUS REPORT

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION, Code BG  
1520 "H" Street, N. W.  
Washington 25, D. C.

Research Grant NsG 116-61  
Terminating date (under no-funds extension): January 31, 1966

KINETICS OF CHEMICAL REACTIONS AT HIGH TEMPERATURES  
by GAS DYNAMIC TECHNIQUES

Host Institution  
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Assisted by:

Dr. David C. Marshall, Postdoctoral Associate (left October 29, 1965)  
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Joint support of Mass Spectrometer - Shock Tube Project  
AFOSR, Mechanics Branch: Mr. Gerald F. Marsters, Research Assistant

FACILITY FORM 602	N66 81239	
	(ACCESSION NUMBER)	(THRU)
	36	None
	(PAGES)	(CODE)
	CR 69558	
	(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

## General Objectives of our Program

In this program we have undertaken to test, confirm and extend some of the laws which control real gas effects at elevated temperatures. The departures from ideal fluid behavior are due to complex modes for energy transfer between molecules, the emission or absorption of large quantities of radiation, and to the transfer of atoms or groups between molecules during collision.

A current pressing question - one which pertains to the chemistry of air and of the planetary atmospheres - is which kinetic factors determine the fragmentation of tri- and tetratomic molecules. The models for these bridge the groups of simple diatoms and of complex polyatomics. We have selected the following for intensive study to ascertain which are the pertinent molecular parameters; in particular,  $C_2N_2$ , HCN, and ClCN. Not only are these present in significant concentrations in rocket motors and are exhausted through nozzles, but also it is readily possible to follow changes in the sample constitution by spectroscopic means; the CN radical concentration may be followed down to a very low level.

We have also chosen two model systems for the study of atom exchange reactions:

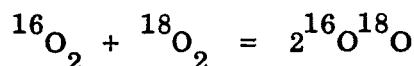
$H_2 + C_2N_2 \rightarrow 2 HCN$ ;  $(D_2 + C_2N_2 \rightarrow 2 DCN)$ ; and the self atom switching process:

$O_2^{16} + O_2^{18} \rightarrow 2 O^{16} O^{18}$ . The latter experiment is designed to test whether the vibrational excitation mechanism which we discovered for the  $H_2 + D_2$  reaction also controls atom switching for the heavier atomic species. Of course, the question of major concern is how to ascertain whether under specified conditions a reaction will be dominated by free radical processes or by group switching processes.

Finally, we became involved in the development of<sup>3</sup> major analytical technique which will permit the study of complex reactions; that is, systems with which one may determine with precision and with a short time resolution the time dependent concentrations of three or more species. We have undertaken to achieve this by coupling a time-of-flight mass spectrometer (which is capable of recording concurrently the 8 - 12 masses with a time resolution of 10 microseconds) to a shock tube, used as the primary reactor for establishing controlled temperatures and densities for gaseous samples. This unit is being set up under the joint support of NASA and the AFOSR, Mechanics Division, in collaboration with Professor Resler of our School of Aerospace Engineering.

### Accomplishments

A measure of success in attaining the objectives of a fundamental research program is the sum of publications in standard journals. Six papers based on the shock tube studies supported by NASA have either appeared or have been accepted for publication; their titles and references are listed below. (Appendix I). One paper has been completed and submitted to the Journal of Chemical Physics, and two reports on partially completed studies are appended (Appendix II). Experimental work on the dissociation of HCN is being continued by Robert Kung, a graduate student in the Department of Chemistry at Cornell. We plan for Mr. Harvey Carroll to continue with his investigation of the exchange reaction



To date he has demonstrated, using our 2" ID single-pulse shock tube, that in approximately equimolar mixtures of  $^{16}\text{O}_2$  and  $^{18}\text{O}_2$  [0.2% in Ar] at total reflected shock densities of about  $10^{-1}$  moles/liter, detectable exchange occurs in 1.5 msec at 1210°K. Above 1400°K, the extent of reaction<sup>is</sup> so high that back reaction must be considered in the kinetic analysis. Shocks were run over the range 1160°K to 1963°K; analysis was performed with a CDC Type 21-103A mass spectrometer (modified). A preliminary value for the activation energy is 45 kcal/mole.

A second measure of achievement is the gain in knowledge by the participants in this program, and the diffusion of this information to the scientific community. This occurs on a personal level through the presentation of invited seminars. Over the period covered by this grant the principal investigator gave such lectures at:

Western Reserve University --- Frontiers of Chemistry Series  
University of West Virginia --- School of Aerospace Engineering  
Gordon Research Conference --- High Temperature Research  
5th Shock Tube Symposium  
Shock Tube Applications to Chemical Kinetics --- Durham - ARO  
Pennsylvania State University --- Department of Chemistry  
Harvard - MIT --- Joint Colloquium in Physical Chemistry  
N.J. and Del. Sections of ACS  
Brooklyn Polytechnic Institute --- Department of Chemistry

Contributed papers were presented at:

10th Combustion Symposium - Cambridge, England  
Various meetings of the American Chemical Society

#### Summary of Recent Constructions

The 6" ID stainless steel shock tube has been further modified. The test section was extended by 6 ft. to provide a longer test period and the entire tube cleaned, carefully aligned and securely clamped to the floor of the laboratory. Mr. Kung, who will continue with the investigation of the pyrolyses of HCN by measuring the time dependent concentration of CN spectrophotometrically, is realigning the optical train. He will use a JACO 8200 spectrophotometer (rather than AMICO 1/4m instrument) to obtain better resolution and more stable operation.

Modifications of the dual channel IR spectrometer have been completed; a second Au-Ge detector has been purchased. We must now construct an appropriate power pack and amplifier for this second IR detector. An all glass-teflon 1" spst is approximately half completed. The purpose was to achieve ultraclean operation, with no metal, grease, or extraneous vapors to produce contamination. This tube will be heatable for continuous

operation at 200°C.

Mr. Marsters is making good progress with the shock tube - mass spectrometer unit. He spent one week at the Mass Spectrometer School at Cincinnati, given by the Bendix Corporation, and returned very well informed of the subtleties in operating our TOF instrument. At present, nearly all the components of the shock tube, transition section and TOF spectrometer have been completed. He has run preliminary shocks in the tube; he developed a technique for recording many spectra for a single run, and made some improvements in the electronics of the TOF spectrometer.

## APPENDIX I

- (a) S. H. Bauer, Shock Waves., Ann. Rev. Phys. Chem., 16, (1965).
- (b) S. H. Bauer and E. L. Resler, Jr., Vibrational Excitation in Some Four-Center Transition States., Science, 146, 1045 (1964).
- (c) David Schofield, Wing Tsang and S. H. Bauer, Thermal Decomposition of ClCN., J. Chem. Phys., 42, 2132 (1965).
- (d) S. H. Bauer and W. S. Watt, The Association of CN in an Expansion Wave, Special Publication: 5th Shock Tube Symposium; accepted for publication in J. Chem. Phys., will appear in February, 1966 issue.
- (e) S. H. Bauer and W. S. Watt, On the Decomposition of  $\text{Cr}(\text{CO})_6$  in Shock Waves., accepted for publication in J. Chem. Phys., will appear in February, 1966 issue.
- (f) G. F. Marsters, S. H. Bauer and E. L. Resler, Jr., Optimized Geometry for Coupling a Mass Spectrometer to a Shock Tube., Special Publication: 5th Shock Tube Symposium.

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Submitted for publication:

ISOTOPE EXCHANGE RATES. IV:  
THE HOMOGENEOUS REACTION BETWEEN  $\text{CH}_4$  and  $\text{D}_2$

W. S. Watt\*, Peter Borrell\*\*, David Lewis and S. H. Bauer

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### ABSTRACT

The rate of exchange of deuterium for hydrogen in the homogeneous gas phase reaction between  $\text{D}_2$  and  $\text{CH}_4$  (highly diluted in argon) was measured behind reflected shocks in a single-pulse shock tube of the "magic hole" design. The studies covered the temperature range  $1440^\circ - 1755^\circ\text{K}$ , at  $\text{CH}_4/\text{D}_2$  ratios from 0.1 to 3.0. The exchange rate was found to be approximately first order with respect to deuterium and one half order with respect to methane and argon. The empirical rate expression and the measured exchange rates cannot be accounted for either by a direct 4-center bimolecular exchange process or by a mechanism involving a dissociation followed by a chain of atom displacement steps. However, these results are readily accounted for by a vibrational excitation mechanism in which the exchange rate is limited by the rate of populating a critical vibrational level for  $\text{D}_2$  (approximately the 5th). The activation energy for exchange is  $52.0 \pm 2.2$  kcal/mole.

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APPENDIX II

THE THERMAL DECOMPOSITION OF HCN

THE HIGH TEMPERATURES PRODUCTION OF HCN FROM  $C_2N_2 + H_2$ ,  
AS STUDIED IN SHOCK TUBES

Preliminary Reports by: Dr. David Marshall and Dr. Peter Jeffers

Assisted by: Messrs. Robert Kung and David Lewis

Under the direction of: Professor S. H. Bauer  
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Contract Number: NsG(116-61) (C.U. 6284)

## ABSTRACT

This report consists of two parts. One concerns the pyrolysis of HCN (highly diluted in argon) by incident shocks (1720° - 2760°K) as followed spectrophotometrically via the rate of production of CN radicals. The second describes a single-pulse shock tube study (reflected shocks, 1070° - 1880°K) of the products found in mixtures of cyanogen, hydrogen and argon at the end of a high temperature dwell period of approximately 1.3 msec. The investigation of HCN decomposition is the more nearly complete work. Mixtures of 0.5%, 1.0%, and 3.0% of HCN in argon were used. The rates were best represented by the empirical expression

$$d(\text{CN})/dt = k_D (\text{HCN})^{0.7} (\text{Ar})^{1.2},$$

with an overall energy of activation of approximately 50 kcal/mole. A possible mechanism is proposed which is capable of accounting for these observations. It involves the formation of vibrationally excited hydrogen cyanide molecules and transient complex species.

The rate of formation of HCN was measured in shock heated mixtures of  $\text{H}_2$  and  $\text{C}_2\text{N}_2$  in argon, of the following compositions: 2/1/97; 2.6/2/95.4; and 0.85/1/98.15. The empirical power rate law deduced from a relatively small number of shocks is

$$d(\text{HCN})/dt = k_4 (\text{H}_2)^2 (\text{C}_2\text{N}_2)^{0.5} (\text{Ar})^1$$

We have not yet found an adequate mechanism which accounts for these results and it is evident that more data must be obtained before these conclusions are fully established. However, our prediction based on the vibrational excitation mechanism for 4-center reactions, that  $\text{D}_2$  would react more rapidly than  $\text{H}_2$  with  $\text{C}_2\text{N}_2$ , has been demonstrated in shocks wherein both  $\text{H}_2$  and  $\text{D}_2$  competed for  $\text{C}_2\text{N}_2$ . Mixtures were exposed to temperatures well below those at which  $\text{H}_2$  -  $\text{D}_2$  exchange occurs at significant rates. The ratios of products found at the end of approximately 1 msec. dwell time were:  $\text{DCN}/\text{HCN} = 6(1050^\circ\text{K})$ ;  $3(1130^\circ\text{K})$ ;  $6(1200^\circ\text{K})$ .



## THE THERMAL DECOMPOSITION OF HCN

### Introduction

Kinetic studies of the thermal decomposition of cyanogen<sup>1</sup>, cyanogen chloride<sup>2</sup>, and cyanogen bromide<sup>3</sup>, using the shock tube technique, have been reported. These reactions were followed by observing the formation of CN radicals spectrophotometrically. In  $C_2N_2$ -Ar mixtures (1700° - 2500°K) dissociation occurs via a direct bimolecular process, involving the carbon-carbon bond rupture; the observed energy of activation was 95 kcal/mole. A similar mechanism was proposed for cyanogen bromide (2500° - 7000°K); the observed  $E_A = 90.5$  kcal/mole. The production of CN radicals by the thermal decomposition of cyanogen chloride (2000° - 2800°K) required a more complex six-step mechanism in which the initially generated CN and Cl radicals participate in subsequent reactions. The energy of activation for the initial dissociation step was found to be 91.5 kcal/mole. Further, there have been many attempts to estimate the heat of formation of the CN radical<sup>1</sup> by determining the enthalpy increment for the dissociation of cyanogen. Values of  $\Delta H_0^0$  range from 105 kcal/mole (appearance potentials of ions in mass spectrometer) to 145 kcal/mole (Knudsen cell and shock tube study), although the most probable value is about 125 kcal. The equilibrium between cyanogen and CN radicals was studied using a shock tube whilst a similar investigation with cyanogen chloride was not possible. The difficulty is due in part to the easy formation of low  $(CN)_m$  polymers at elevated temperatures.

This reports on a study of the kinetics of the thermal decomposition of hydrogen cyanide over the temperature range 1720° to 2760°K. The magnitude of the CN concentration was followed with microsecond resolution by absorption spectroscopy at the (0, 0) band head of the  $B, {}^2\Sigma^+ \rightarrow X, {}^2\Sigma^+$  transition ( $\lambda$  3883Å<sup>0</sup>). Preliminary results also indicate that, with the present apparatus, equilibrium studies can be made with a 0.1% mixture of HCN in argon at 3000°K.

## Experimental

Hydrogen cyanide was prepared in a conventional vacuum line by the reaction of sulphuric acid (55% w/w) on potassium cyanide<sup>4</sup>. The impure gas was passed through anhydrous calcium chloride and stored for a day over phosphorus pentoxide at -10°C. The hydrogen cyanide was cooled to -78°C in an acetone/dry ice mixture and then thoroughly degassed. A mass spectral analysis of the final product showed no impurities. The argon (Airco) had a stated purity of 99.998%. Mixtures of 0.5, 1 and 3% hydrogen cyanide in argon were prepared in 50 gallon tanks. The samples were allowed to mix for two days before use.

The shock tube and instrumentation are shown diagrammatically in Figure 1. The 6 inch i.d. stainless steel shock tube has a total length of 28 feet with a 6 foot driver section. The quartz observation windows were set 18 feet downstream from the diaphragm. A 4 foot extension of the tube beyond this point allowed an observation time between 1.8 msec at 1825°K and 1.5 msec at 2375°K before disturbance by reflected waves. The quartz windows were cylindrical, 15 mm. diameter, mounted horizontally so that the inner faces were flush with the inside wall of the tube. The diaphragms were of Mylar, scribed to varying depths to give the required breaking pressure. Helium was used as the driver gas at initial pressures between 20 and 110 lb./sq. in.

The CN concentration was measured by monitoring the absorption intensity at the (0,0) band of the  $B, {}^2\Sigma^+ \rightarrow X, {}^2\Sigma^+$  transition of CN at  $3883\text{\AA}^0$ . A discharge lamp<sup>1</sup> was used as a characteristic source. It was filled to a pressure of 11 mm. with a mixture consisting of 30% n-butane, 20% nitrogen and 50% argon, and operated by triggering a 17 kV high voltage supply across the electrodes. The CN emission at  $3883\text{\AA}^0$  assumed an almost constant intensity for 1.5 milliseconds, after an initial rise time of 600 microseconds.

An Aminco grating monochromator, f.l. 250 mm., with a 1200 lines/mm. grating was used as a narrow band filter. The  $30\mu$  entrance and exit slits correspond to a bandwidth of  $1\text{\AA}^0$  at the head of the P branch. From the Fortrat diagram for the CN band at  $3883\text{\AA}^{0.5}$ , this width extends from  $J = 19$  to  $J = 38$ .

Light from the discharge lamp was focused to a parallel beam by a quartz lens before passing through the tube. The emerging beam was defined by two slits, 1 mm. wide separated by a distance of 26 cm., before being brought to a point focus on the entrance slit of the monochromator by a second lens. The slits, positioned against the quartz window and the second lens, limited the width of the region observed in experimental section. A IP 28 photomultiplier tube was mounted against the exit slit of the monochromator. A potential of 560 volts applied across the electrodes gave a maximum output signal of 1.1 volt during the flat portion of the lamp output. The signal was sent, via a Dual Trace Type CA plug-in unit to a Tektronix 535 oscilloscope. The output of a Kistler pressure transducer mounted 21 cm. beyond the quartz windows was fed to the second channel. The screen trace was recorded on Polaroid film.

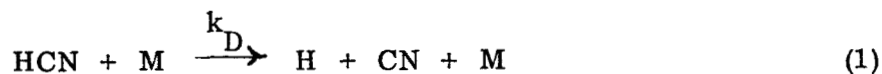
Shock velocities were determined from signals derived from four platinum film heat-transfer gauges located along the length of the tube. The signals were displayed on a raster, (Tektronix 513D oscilloscope), upon which were superposed  $10\mu\text{sec}$  markers. The trigger signal was derived from a shock-mounted barium titanate piezo-electric crystal<sup>6</sup>, connected via amplifiers and a time-delay unit to the two oscilloscopes and the high voltage supply for the discharge lamp. The pressure of the hydrogen cyanide-argon mixture in the driver section was varied between 6 and 20 mm. Between runs the tube was pumped down to  $2 \times 10^{-4}$  mm. The leak rate was 0.05 micron/minute so that the background pressure in

any experiment never exceeded 1 micron.

The incident shock velocity ( $U_1$ ) and the ratio of densities ( $\phi$ ) behind and in front of the shock were computed at 25°K intervals over the required range. Values of the coefficients for the enthalpy polynomials were obtained from the Los Alamos file. To test for the possibility of emission, shocks were made at 2600°K in 3% HCN without the discharge lamp in operation. No emission was observed except at a time when there was an appreciable leak rate of air into the tube. A typical photographic trace of absorption due to the formation of CN radicals is shown in Figure 2, for 3% hydrogen cyanide in argon at 2146°K.  $I_0$  and  $I$ , the intensities before and during the shock, were measured at 50  $\mu$ sec. intervals;  $\log(I_0/I)$  was plotted against laboratory time, as shown in Figure 3. This graph clearly shows an induction period; that is, after the arrival of the shock there is an initial period of approximately 200  $\mu$ sec. during which no CN radicals were observed. The curvature that follows is due to a steady increase in the rate of formation of CN radicals. Thereafter the plot of  $\log(I_0/I)$  vs  $t$  is strictly linear, showing that the rate of production was constant. The apparent induction period and the time interval between this and the attainment of a constant rate decreased as the temperature increased. At 2462°K, the induction period was 60  $\mu$ sec and there was no observable curvature. Additional experimental details are summarized in Table I.

#### Interpretation of the Kinetic Data

If the only reaction which can lead to the production of CN radicals were



then we would observe,

$$\begin{aligned} d[\text{CN}]/dt &= k_D [\text{HCN}] [\text{M}] = k_D \rho^2 (X_{\text{HCN}})(X_{\text{M}}) \\ &= \alpha d(\ln I_0/I)/dt \end{aligned} \quad (2)$$

where  $\alpha$  is a constant involving the absorption coefficient, path length, etc.<sup>7</sup>;  $\rho$  = total density;  $X_{\text{HCN}}$  = mole fraction of hydrogen cyanide;  $X_{\text{M}}$  = mole fraction of colliders, essentially the mole fraction of argon;  $k_{\text{D}}$  = decomposition rate constant. When  $k_{\text{D}}$  is expressed in Arrhenius form,  $R \equiv \ln[(1/\rho^2) d(\ln I_0/I)/dt] = -E/RT + \text{constant}$  (for a specified mixture). The slope of a plot of  $R$  vs  $1/T$  gives the activation energy. The complete set of results is reproduced in Figure 4. Two distinct sets of data are shown, with an appreciable displacement between them. The second set contains no results with the 1% HCN mixture. The displacement appeared after the monochromator was shifted and then readjusted during the course of the experiments. Because of the coarseness of the  $\lambda$  drive, it was not possible to reset the instrument exactly to the same position on the band head. A least squares calculation of the slopes gives the following values for the energy of activation:

	Set I	Set II
3% HCN	49.0	53.9
1% HCN	(42.1)	—
0.5% HCN	48.3	57.7

The most significant point of these results is that the energy of activation for the production of CN radicals is much lower than the expected value for the direct dissociation to  $\text{H} + \text{CN}$ . [ $\Delta H_{\text{diss}}^{\circ}(2000^{\circ}\text{K}) = 131 \text{ kcal/mole}$ , or  $121 \text{ kcal/mole}$ ]. There is also an appreciable displacement of the lines passing through the data points for the 3% and 0.5% mixtures in each set of results. This is clear cut experimental evidence that the generation of CN is not entirely due to the expected bimolecular dissociation reaction of hydrogen cyanide. A more complex mechanism is required to account for these observations.

An empirical equation for the rate of formation of CN,

$$d[\text{CN}]/dt = k(\text{HCN})^m (\text{Ar})^n \quad (3)$$

can be derived from our data. If we substitute in eq. (2) for  $d[\text{CN}]/dt$ ,  $(\text{HCN})$  and  $(\text{Ar})$  then,

$$\log \left[ \frac{d(\ln I_o/I)}{dt_p} \right] + \frac{E}{2.303 RT} = (m+n) \log (p_1 \phi) + m \log X_{\text{HCN}} + n \log X_{\text{Ar}} + \text{constant}, \quad (4)$$

where  $p_1$  is the sample pressure and  $\phi = p_2/p_1$ . For a sample of fixed composition, a

plot of  $\log \left[ \frac{d(\ln I_o/I)}{dt_p} \right] + \frac{E}{2.303 RT}$  against  $\log (p_1 \phi)$  gives a line with slope equal

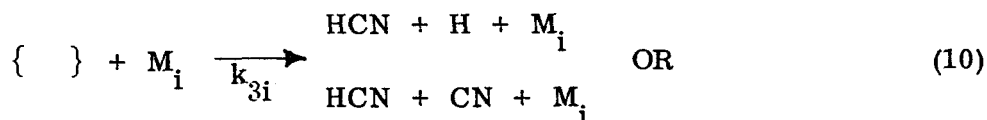
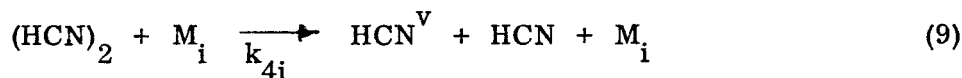
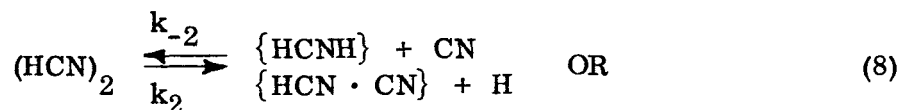
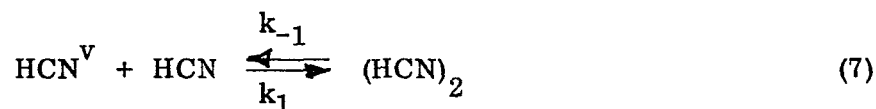
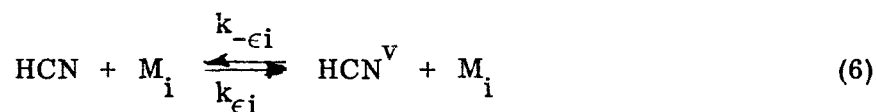
to  $(m+n)$ , the total order of the reaction. These are shown in Figures 5 and 6 for 3% HCN (sets I and II) and 0.5% (set I), for which  $E$  was assumed to be 47.4 kcal/mole. The other sets show too much scatter to give a meaningful estimate for the slope. The average total order is therefore  $1.9 \pm 0.2$ . Knowing  $(m+n)$ , it is possible to evaluate  $m$ . Assuming

that  $X_{\text{Ar}}$  is constant for the three mixtures, a plot of  $A \equiv \log \left[ \frac{d(\ln I_o/I)}{dt_p} \right] + \frac{E}{2.303 RT} - 1.8 \log (p_1 \phi)$  against  $\log X_{\text{HCN}}$  has  $m$  for its slope. An average value of  $A$  was calculated from all the data points for each mixture. The plot is shown in Figure 7, from which  $m = 0.7$  (set I) and 0.6 (set II). Thus, the empirical power rate equation is

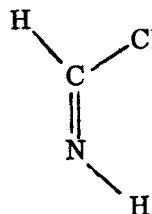
$$d[\text{CN}]/dt = k_D [\text{HCN}]^{0.7} [\text{Ar}]^{1.2} \quad (5)$$

Final reduction of all the data points on the basis of eq. (5) gives an Arrhenius plot, as shown in Figure 8. A least squares calculation of the slope leads to activation energies 44.3 (set I) and 53.7 kcal/mole (set II). These low  $E_{\text{act}}$ 's, and the non-integral values of  $m$  and  $n$  strongly support the hypothesis that CN radicals are produced from hydrogen cyanide by a multi-step mechanism.

In the search for an acceptable mechanism we have considered and discarded numerous schemes based on the production of free radicals and chains. None which we conceived led to the observed concentration dependence, nor were the estimated activation energies low enough to be acceptable. However, we have found a "successive excitation" mechanism involving dimers which does give a rate expression of suitable form, and suggests how the observed activation energy could be less than the bond dissociation energy. This type of mechanism may be generally applicable to the dissociation of HX compounds (X = F, Cl, OH, NH<sub>2</sub>, as well as CN).



$\text{M}_i = \text{Ar}$  ( $i = 1$ ) ;  $\text{HCN}$  ( $i = 2$ ) in eqs. (6), (9), and (10). We propose that  $(\text{HCN})_2$  is a highly excited [by about 50 kcal/mole] but classically possible specie, generated by the addition of  $\text{HCN}^v$  at the  $\text{C} \equiv \text{N}$ ,



for choosing between the upper and lower products. Only those  $(\text{HCN})_2$  complexes generated from vibrationally excited molecules have sufficient energy to dissociate according to eq. (8); the necessary energy for bond breaking is thus provided by the stabilizing energy of the residue. Note that  $(\text{HCN})_2$  can be quenched via eq. (9). This is an essential step; if omitted the calculated rate expression does not agree with the one observed. On applying the steady state condition in  $\text{HCN}^V$ ,  $(\text{HCN})_2$  and  $\{ \}$ , and on introducing several other approximations which may be readily justified, one obtains

$$\frac{d(\text{CN})}{dt} = \frac{k_1 k_2 \sum k_{ei} (M_i) \sum k'_{3i} (M_i) (\text{HCN})^2}{(k_{-2} \text{CN} + \sum k_{3i} M_i) [(\sum k_{-ei} M_i + k_1 \text{HCN}) (k_{-1} + k_2 + \sum k_{4i} M_i) - k_1 k_{-1} \text{HCN}]} \quad (11)$$

$$\frac{d(\text{CN})}{dt} \approx \frac{\sum k_{ei} (M_i) k_1 k_2 (\text{HCN})^2}{(k_1 \text{HCN} + \sum k_{-ei} M_i) (k_{-1} + k_2 + \sum k_{4i} M_i) - k_1 k_{-1} \text{HCN}} \quad (12)$$

Note that the dependence on  $\sum k_{3i} M_i$  cancelled from the numerator and denominator upon introducing the assumption that  $\sum k_{3i} M_i \gg k_{-2} \text{CN}$ . The net dependence of  $d(\text{CN})/dt$  on density is of the form  $\rho^2/(a + b\rho)$ ; if  $\sum k_{4i} M_i$  were deleted, only a quadratic dependence would be allowed. Further, it is clear that the dependence on  $(M)$  could be slightly greater than unity (eq. 11); that on  $(\text{HCN})$  could be less than unity only if one assumes that  $k_{4,2}(\text{HCN}) > k_{4,1}(\text{Ar})$  while  $k_1(\text{HCN}) \gg \sum k_{-ei} M_i$ .

Prior to the establishment of the steady state condition there is an induction period during which the population of  $\text{HCN}^V$  is being built up. This is followed by the measurable slow increase in  $(\text{CN})$ , which finally attains a uniform growth. A third region can be anticipated when equilibrium between the  $\text{HCN}$  and  $\text{CN}$  radicals is approached; experimentally  $\ln(I_0/I)$  levels off and attains a constant value. There are other interesting aspects of this mechanism such as the possibility that  $\text{CN}$  or  $\text{H}$  tend to inhibit the dissociation by reversal of eqs. (8) and

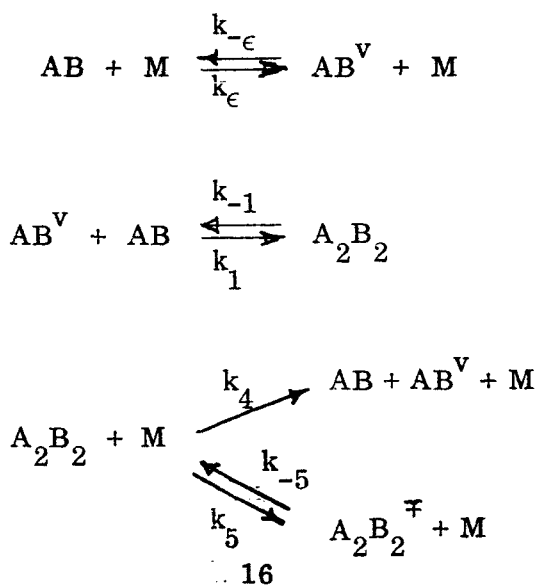


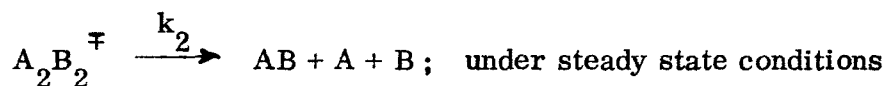
and (10). The inverse of the entire process [i.e. the recombination reaction] starts with a 3-body process, which presumably has a favorable probability for association due to the relative stability of  $\{ \quad \}$ . The reaction is thus autocatalytic.

Besides accounting for the observed induction period, this mechanism is indirectly supported by a preliminary analysis of the concentration changes for CN during the initial transition to the steady state condition. Somewhat arbitrary estimates of initial slopes gave values for the initial net rate constants, calculated on the assumption that the reaction was first order with respect to initial HCN and Ar. The approximate  $(E)_{in} \approx 75$ . This we interpret as an indication that the direct bimolecular dissociation contributes significantly to the production of CN during the initial stages, prior to the establishment of the dominant role by successive excitation mechanism.

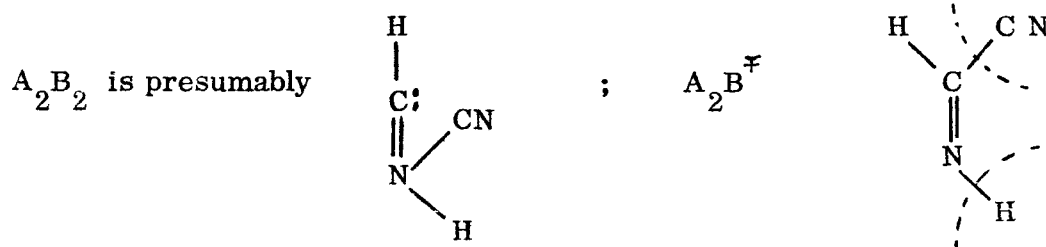
Preliminary runs were also made with 0.1% HCN mixtures, at sufficiently high temperatures so that the equilibrium concentration of CN was nearly attained during the test period. These data were reduced in the usual way to provide an estimate of  $\Delta H_{\text{diss}}^{\circ}$  ( $\approx 84$  kcal/mole).

It is worth noting that there is a variant of the proposed mechanism which also leads to the observed density dependence. In general terms ( $A = CN$  ;  $B = H$ ):





$$\frac{dA}{dt} = \frac{k_{\epsilon} k_1 k_2 k_5 (AB)^2 (M)^2}{(k_{-\epsilon} M + k_1 AB) [k_{-1} k_2 + k_2 M (k_4 + k_5) + k_{-5} M (k_{-1} + k_4 M)]} \propto \frac{\rho^3}{1 + \alpha \rho + \beta \rho^2}$$



### Continuation of Program

The driven section of the 6" shock tube has now been extended, and the entire tube realigned. This will permit a longer test time and more reproducible operation. The entire optical train is being realigned. We will use a JACO 8200 1/2m spectrophotometer, well insulated, to provide both higher spectral resolution and greater precision of resetting the wavelengths transmitted.

First on the program is the re-determination of  $\Delta H_{\text{diss}}^0$  for HCN, using 0.1% mixtures. To check the proposed mechanism rates will be measured with the lowest possible concentrations. Finally, we hope to set up a computer program for the initial stages of the reaction, so that we may obtain estimates of the individual rate constants from the measured induction times, detailed concentration dependencies, etc.

## REFERENCES

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4. Handbook der Präparativen Anorganischen Chemie, p.500.
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7. W. Tsang et al (ref. 1) found for a 1 1/2 ID tube,  $\mu l = 3.77 \times 10^5$  liters/mole, at the band head, essentially independent of temperature. For this tube, the corresponding value is therefore approximately  $1.51 \times 10^6$  liters/mole.

TABLE I. Typical Experimental Values for HCN Pyrolytic Shocks

Run No.	Composition HCN/Ar	$p_1$ (mm)	$U_1$ mm/ $\mu$ sec	$\rho_2/\rho_1$	$T_2$ (°K)	Final Slope (sec <sup>-1</sup> )	Initial Slope (sec <sup>-1</sup> )
291	0.5%	7.0	1.625	3.609	2620	907.50	
329	HCN	9.0	1.605	3.607	2562	882.19	
371		10.2	1.568	3.580	2458	940.74	171.43
369		12.6	1.546	3.568	2398	838.71	180.00
333		13.3	1.484	3.533	2231	377.42	55.26
355		16.3	1.472	3.525	2198	578.79	33.33
339	1%	10.0	1.575	3.581	2462	1110.53	
341	HCN	12.0	1.527	3.555	2331	948.57	
337		13.0	1.470	3.521	2180	510.00	
259		14.0	1.355	3.472	1890	172.58	
257		15.5	1.342	3.461	1858	125.44	
253		19.0	1.282	3.411	1718	104.65	
407	3%	9.2	1.669	3.790	2654	1014.49	
435	HCN	9.8	1.646	3.778	2591	958.73	
419		12.2	1.572	3.735	2390	755.56	
401		13.7	1.554	3.723	2340	518.84	
433		14.0	1.521	3.702	2254	354.24	
427		16.3	1.492	3.681	2177	351.02	
429		18.9	1.447	3.648	2063	161.64	

## LEGENDS FOR FIGURES

Figure 1. Schematic of experimental set-up.  
KG (Kistler quartz pressure transducer)

Figure 2. Typical oscillogram record.

Figure 3. Absorption as a function of lab time. Note the clear indication of an induction period.

Figure 4. Initial approximation for the activation energy.

$$R \equiv \ln \left[ \left( \frac{1}{\rho^2} \right) \frac{d(\ln I_o/I)}{dt} \right]$$

$$= \log \left[ \frac{2.303 \frac{d \log (I_o/I)}{dt_p}}{p^2 \phi^2} \right] - \log (X_{\text{HCN}} X_{\text{Ar}})$$

since  $\phi = \rho_2/\rho_1$

Figure 5. Determination of total order (3%). The larger number of points available in set II bias the average toward 1.8 [Reduced on basis of  $E = 47.4$  kcal/mole].

Figure 6. Determination of total order (0.5%). Here set II has too much scatter. [Reduced on basis of  $E = 47.4$  kcal/mole].

Figure 7. Determination of partial order, with respect to (HCN). [These points were reduced on the assumption that the total order was 1.8, and that  $E = 47.4$  kcal/mole].

Figure 8. Final reduction of all data points, to establish best value for the overall activation energy. The power rate expression used was based on

$$\frac{d(\text{CN})}{dt} = k (\text{HCN})^{0.7} (\text{Ar})^{1.1}$$

Points designated by  $\square$  were not used in the least squares analysis.

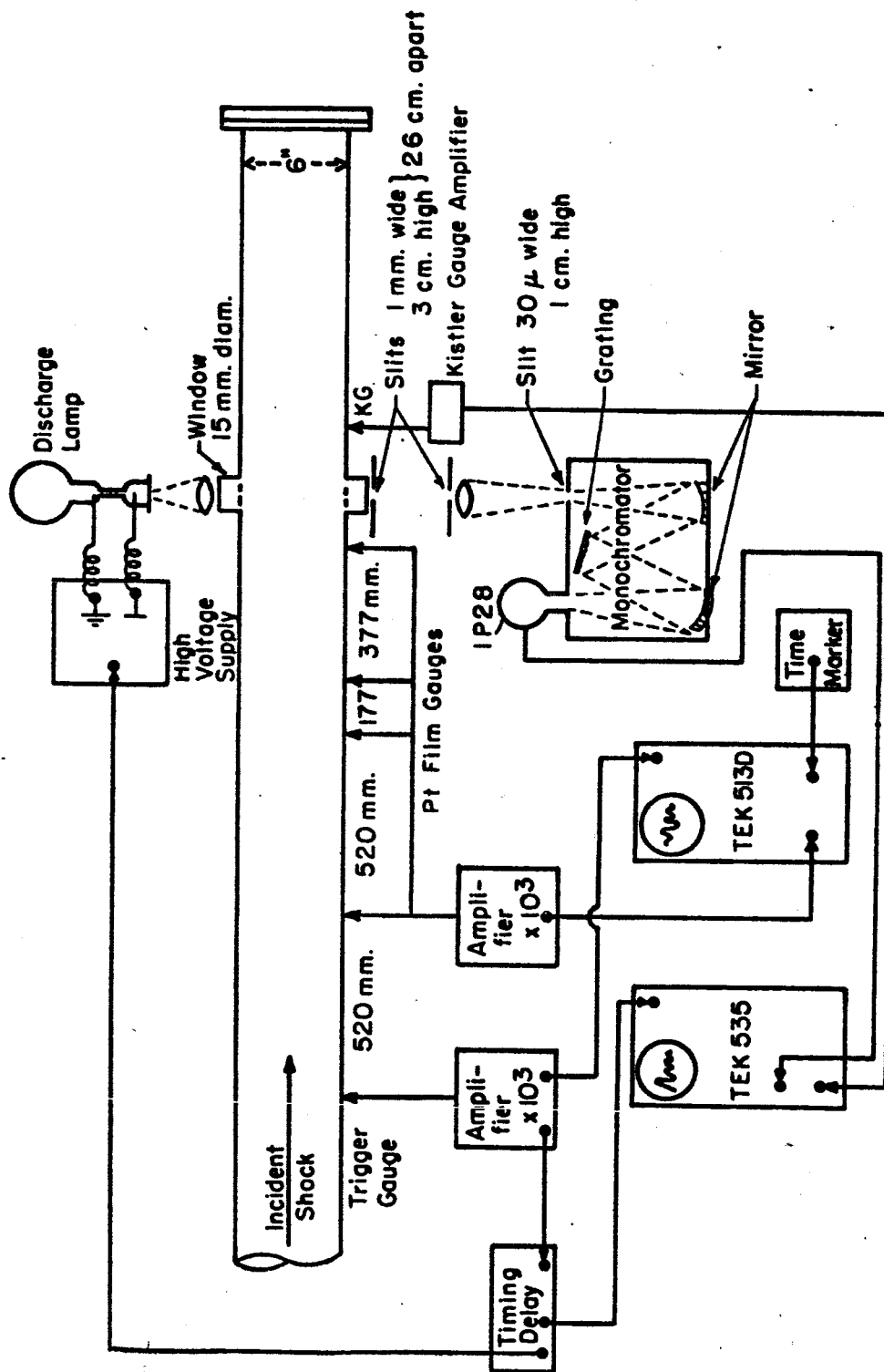


Figure 1 - HCN pyrolysis

Fig. 2

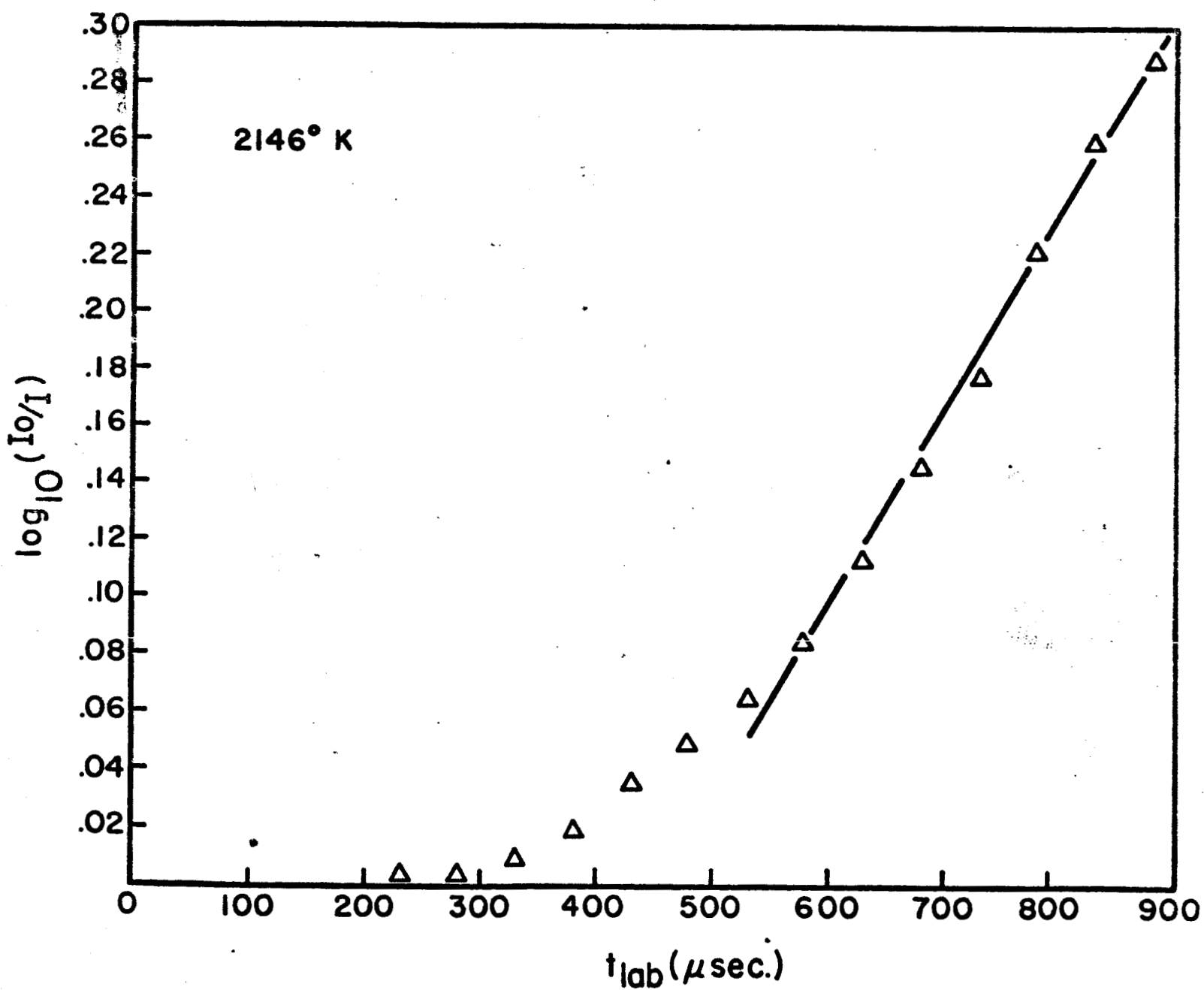
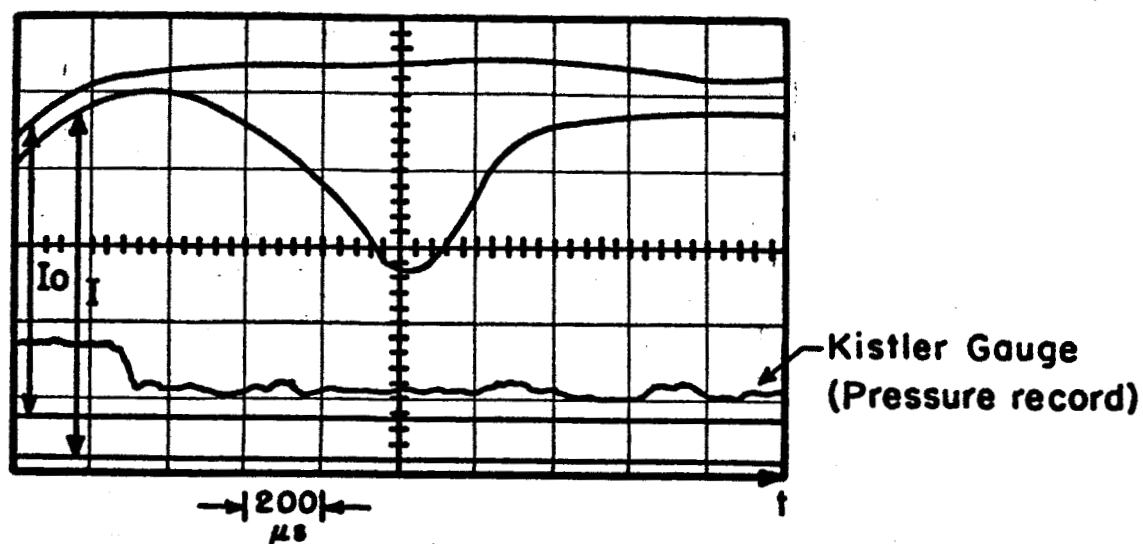
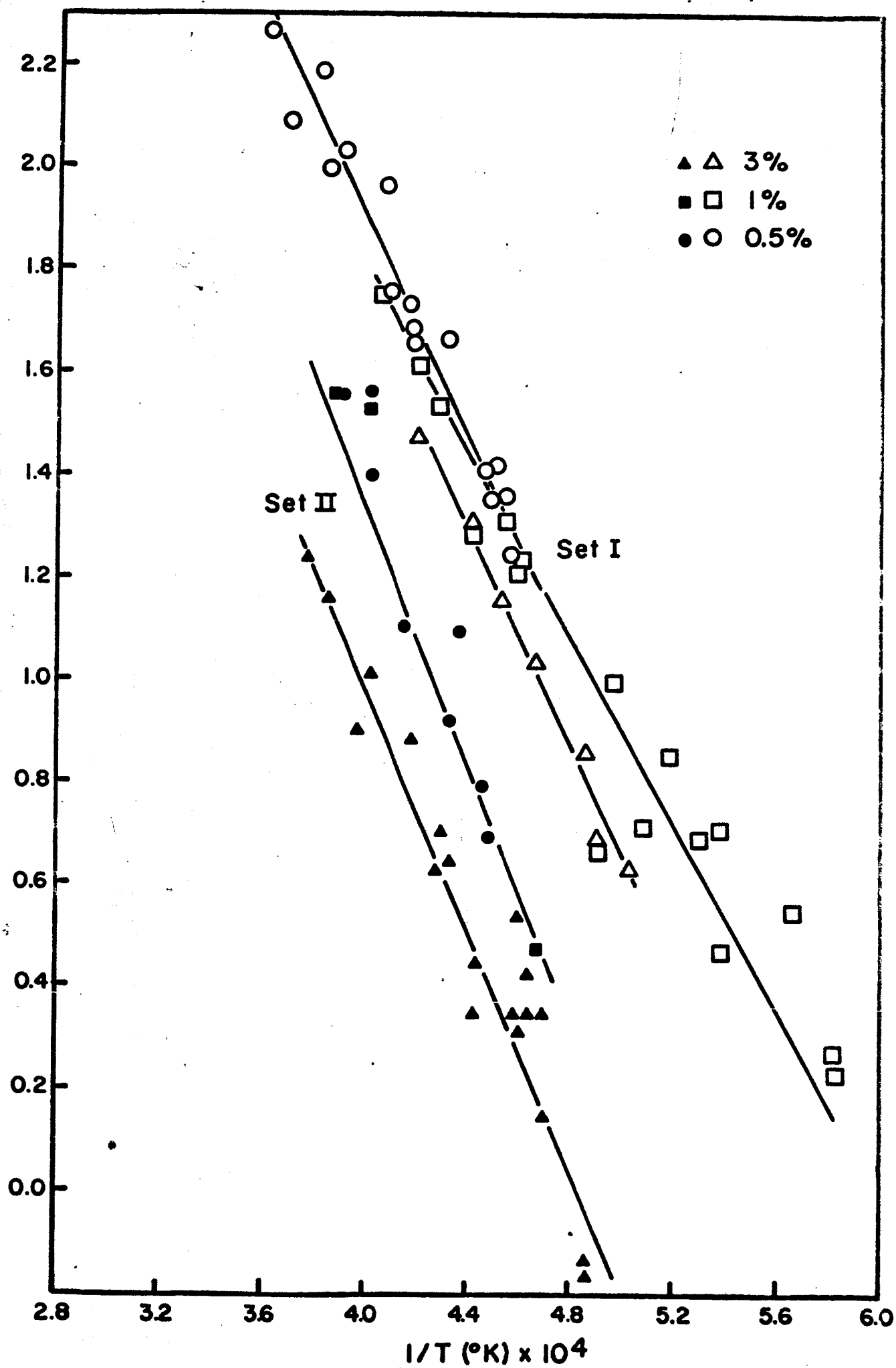


Fig. 3

$$\log \left[ \frac{2.303 \, d \log(I_0/I)}{p^2 \phi^2 \, dt_p} \right] - \log(X_{\text{HCN}} X_{\text{Ar}})$$





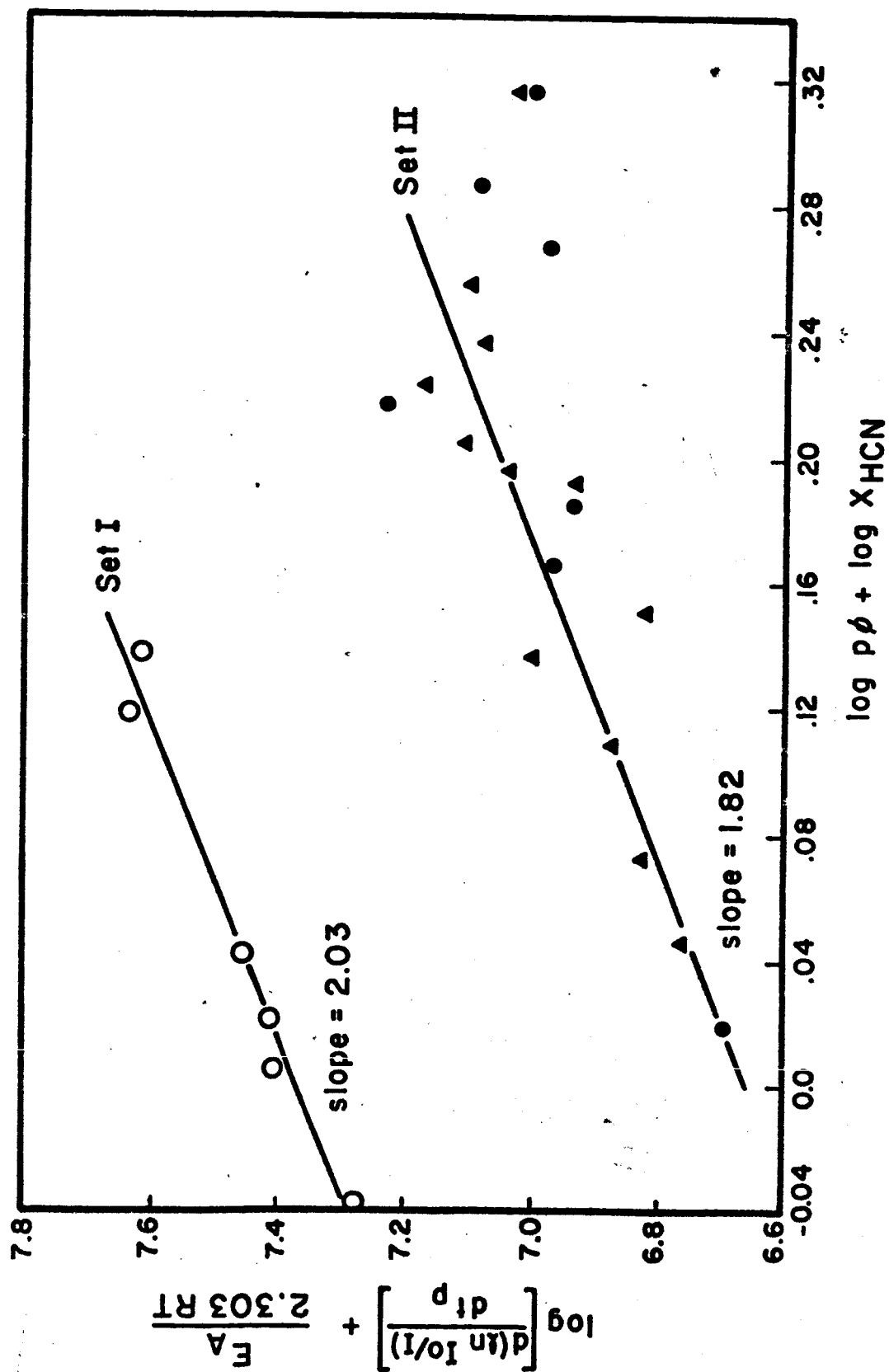


Figure 5 - HCN pyrolysis

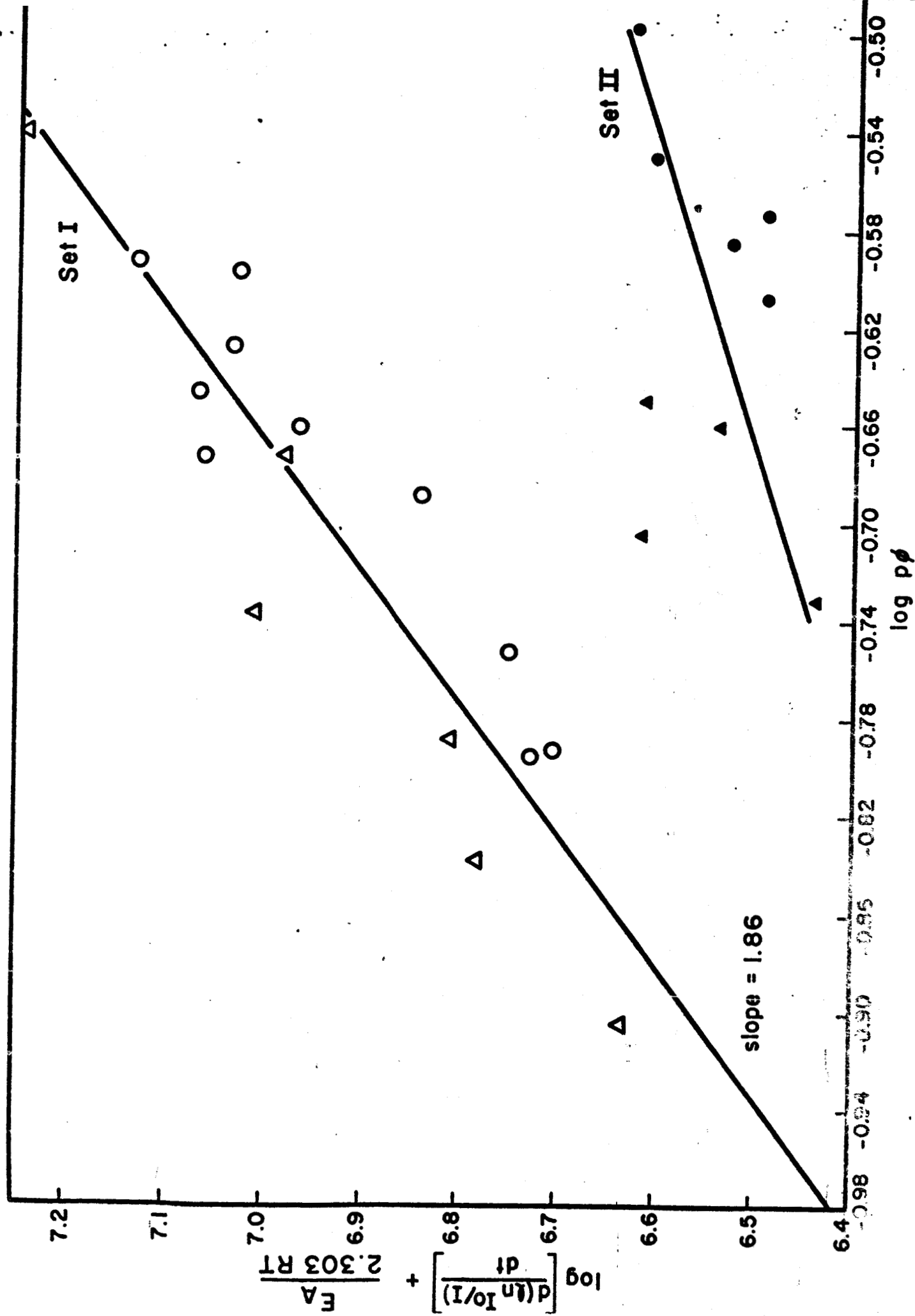
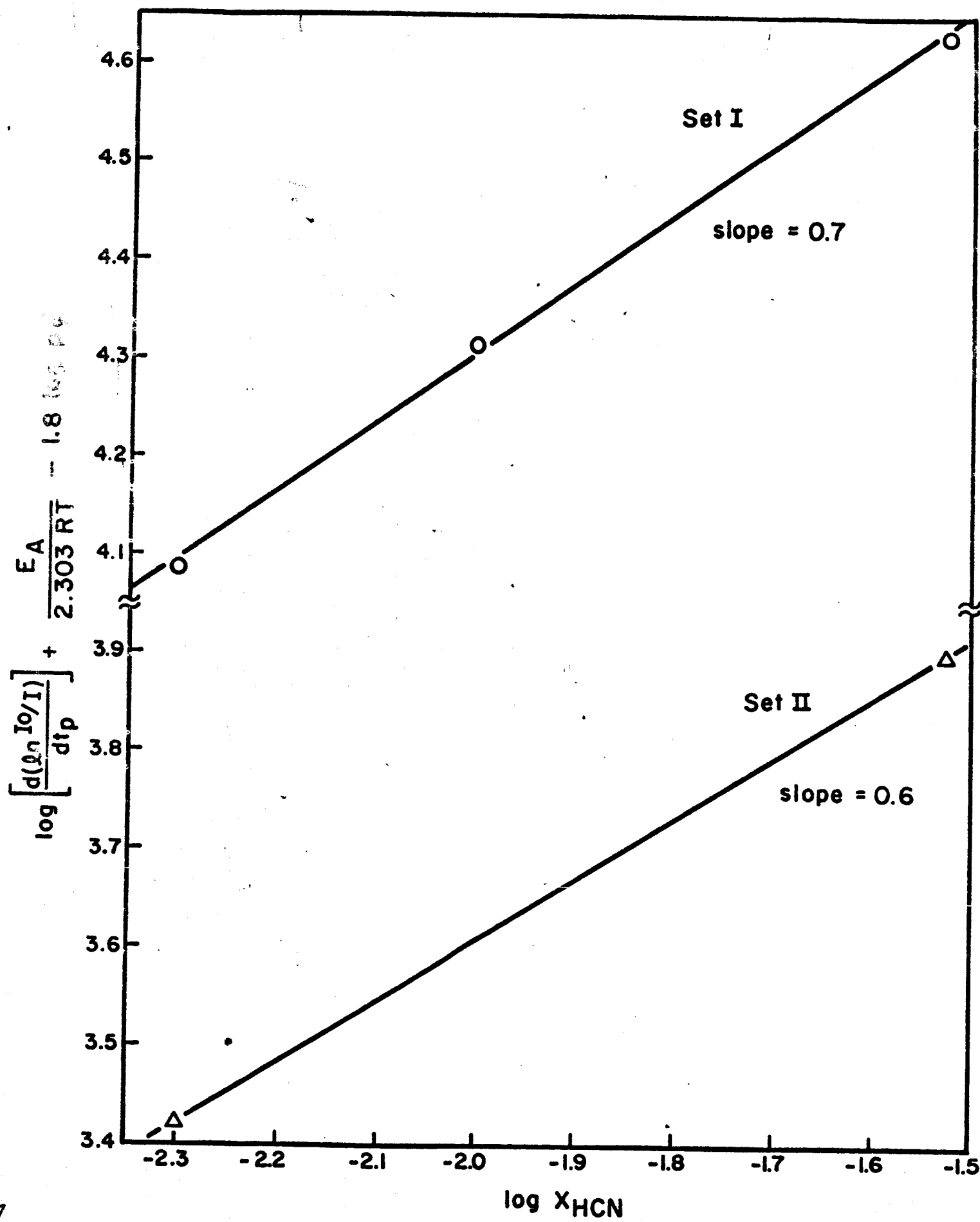
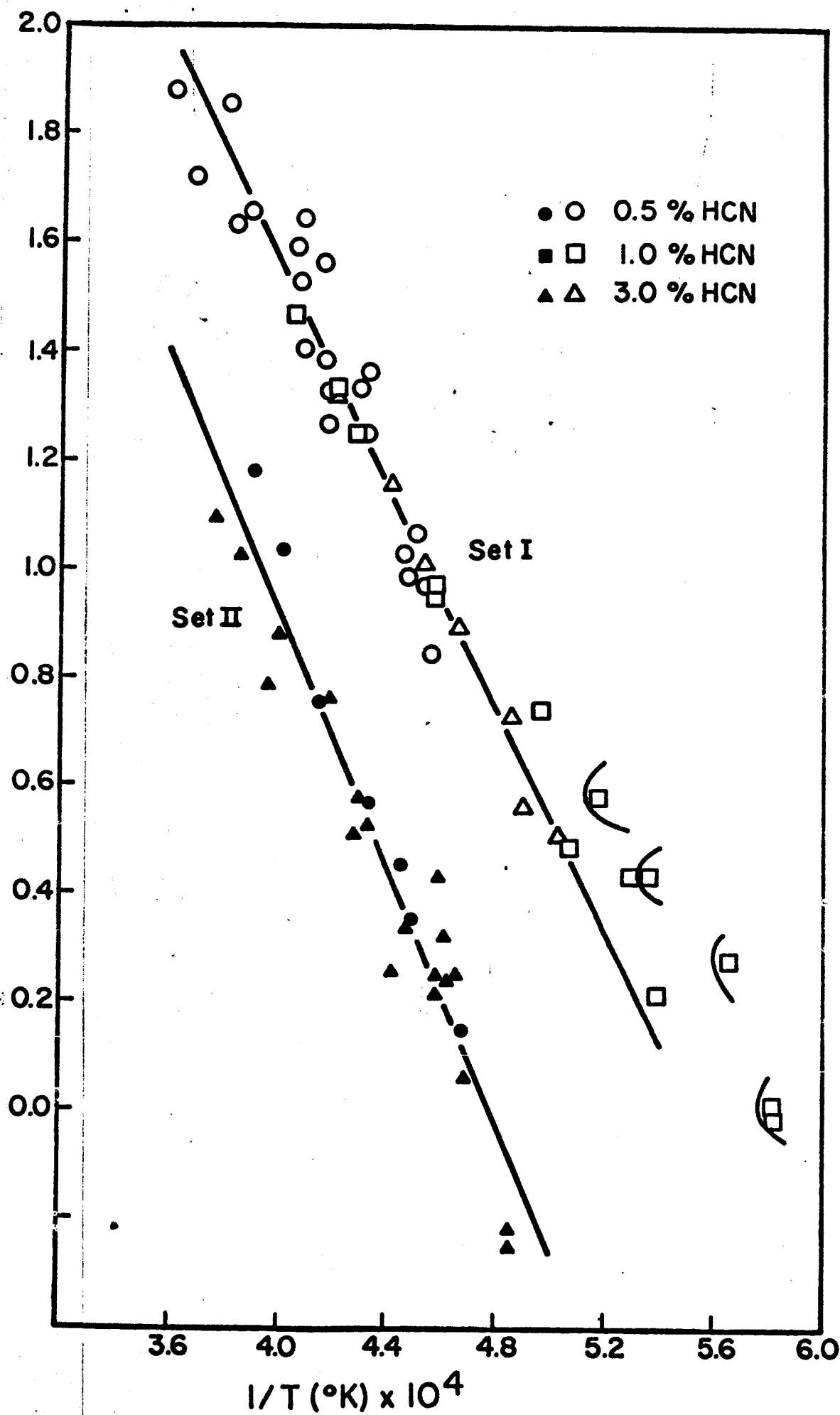


Figure 6 - HCN pyrolysis



$$\log \left[ \frac{2.303 d \log(I_0/I)}{dt p} \right] - 1.8 \log p \phi - 0.7 \log \chi_{\text{HCN}} - 1.1 \log \chi_{\text{Ar}}$$



## THE HIGH TEMPERATURE PRODUCTION OF HCN

Mixtures of 2%  $\text{H}_2$  - 1%  $\text{C}_2\text{N}_2$ ; 2.56%  $\text{H}_2$  - 2%  $\text{C}_2\text{N}_2$ ; and 0.85%  $\text{H}_2$  - 1%  $\text{C}_2\text{N}_2$  were heated in a 1 1/2" single-pulse shock tube to reflected shock temperatures (1070° - 1880°K). Samples of the shocked gas were withdrawn and analyzed with a mass spectrometer. For comparison a sample of 2%  $\text{C}_2\text{N}_2$  in argon (no hydrogen) was shocked to 1730°K and its mass spectrum recorded. Since the spectra of unshocked and shocked  $\text{C}_2\text{N}_2$  were identical, it is evident that there was no thermal degradation of the  $\text{C}_2\text{N}_2$  at the temperature employed in this study. The mass balance of HCN generated in the ( $\text{C}_2\text{N}_2 + \text{H}_2$ ) runs and of the  $\text{H}_2$  and  $\text{C}_2\text{N}_2$  used always checked well. Table I indicates the extent of reaction observed.

In preparing samples to be shocked, a 5 liter bulb was filled to a pressure of about 10 cm. with  $\text{C}_2\text{N}_2$ . The  $\text{C}_2\text{N}_2$  was then frozen into a liquid  $\text{N}_2$  trap and evacuated to remove air which was found as an impurity. The  $\text{C}_2\text{N}_2$  was finally allowed to fill the sample bulb to the desired pressure, after which  $\text{H}_2$  and Ar were added.

Four possible mechanism for the reaction were considered:

- (a) Vibrational excitation of  $\text{H}_2$  followed by a very rapid reaction with  $\text{C}_2\text{N}_2$  [1st order  $\text{H}_2$ ; 1st order in Ar].
- (b) Direct bimolecular reaction of  $\text{H}_2$  and  $\text{C}_2\text{N}_2$  [1st order  $\text{H}_2$ , and 1st order  $\text{C}_2\text{N}_2$ ].
- (c) Reaction second order in  $\text{H}_2$  [zero order in  $\text{C}_2\text{N}_2$ , Ar].
- (d) Reaction second order in  $\text{H}_2$ , half order in  $\text{C}_2\text{N}_2$ .
- (e) Reaction is second order in  $\text{H}_2$ , half order in  $\text{C}_2\text{N}_2$  and unit order in argon.

As indicated by Table I, the conversions were quite high (although equilibrium was not so closely approached to make the reverse reaction troublesome), suggesting that best results would be obtained with an integrated form of the rate expression:

$$(a) \quad \text{Assuming } k_x \gg k_{-x}, \quad \ln \frac{b}{b-x} = k_{\epsilon} \rho_5 \tau,$$

where  $b = [H_2]_0$ ,  $x = [HCN]/2$ . The same expression results with no assumption if  $[C_2N_2]_0 = [H_2]_0$ .

$$(b) \quad \frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)} = k_f \tau, \quad \text{where } a = [C_2N_2]_0$$

$$(c) \quad \frac{2}{b-x} - \frac{2}{b} = k_2 \tau$$

$$(d) \quad \left[ \frac{1}{b-x} - \frac{1}{b} \right] + \frac{1}{a-b} \ln \frac{a(b-x)}{b(a-x)} = \frac{a^2 - 2ab + b}{2(a-b)} \tau k_3$$

The usual Arrhenius plots for the first two mechanisms show considerable scatter; the third is given in Figure 1. In Figure 2 the differential form for the rate was plotted, with a pre-exponential factor  $10^{14}$  giving an activation energy of 37.2 kcal/mole. The slope determined from the other two figures is approximately the same. Figure 3 corresponds to assumption (e). None of these provides an acceptable basis for reducing the data. The best empirical power expression is given by (e),

$$\frac{d(HCN)}{dt} = k_4 (H_2)^2 (C_2N_2)^{1/2} (Ar)^1$$

Justification for this total order of 3.5 is given in Figure 4. It is possible that this is the inverse of the mechanism we proposed above for the dissociation of HCN. We have not yet

pursued the consequences of that proposal to take into account the subsequent reactions of CN and H; this must be done to check this point.

The obvious next phase in a more detailed study of this system would be the accurate determination of the total and partial orders for an empirical power rate expression. The work should probably be performed at low enough temperatures to permit use of a differential rate expression.

TABLE I

Mixture	T <sub>5</sub>	$\tau$	% HCN	$\Delta$ [HCN]	$\frac{\text{moles}}{\text{liter}}$	$\rho_5$
2% H <sub>2</sub> - 1% C <sub>2</sub> N <sub>2</sub>	1090	1300 $\mu\text{sec}$	0.129	2.68 x 10 <sup>-5</sup>		20.8 x 10 <sup>-3</sup>
	1195	1320	0.83	16.1	"	19.4
	1252	1410	1.15	19.7	"	17.1
	1335	1410	1.53	22.8	"	14.9
	1488	1450	1.77	22.5	"	12.7
	1580	1410	1.81	21.0	"	11.6
	1595	1410	1.82	20.0	"	11.0
	1879	1320	1.84	16.6	"	9.04
2.56% H <sub>2</sub> - 2% C <sub>2</sub> N <sub>2</sub>	1190	1320	0.934	16.3	"	17.5
	1494	1500	3.42	40.4	"	11.8
0.85% H <sub>2</sub> - 1% C <sub>2</sub> N <sub>2</sub>	1072	1300	0.003	0.06	"	20.4
	1141	1310	0.011	0.24	"	18.6
	1265	1360	0.106	1.81	"	17.1
	1378	1430	0.394	5.95	"	15.1
	1518	1500	0.531	6.80	"	12.8
	1665	1360	0.958	9.69	"	10.1
	1843	1200	1.15	10.2	"	8.85



## LEGENDS FOR FIGURES

Figure 1. Amount of HCN produced vs  $1/T$  on the basis of an integrated expression, second order in  $H_2$  and zero order in  $C_2N_2$ , Ar. [mechanism (c)]

$$k_c = 10^{12} \exp(-35,400/RT)$$

Figure 2. Differential plot based on mechanism (d).

$$\frac{(HCN)}{\tau} = k_3 <H_2>^2 <C_2N_2>^{1/2}$$

$$k_3 = 1.4 \times 10^{14} \exp(-37,200/RT)$$

Figure 3. Plot of points reduced according to the differential form

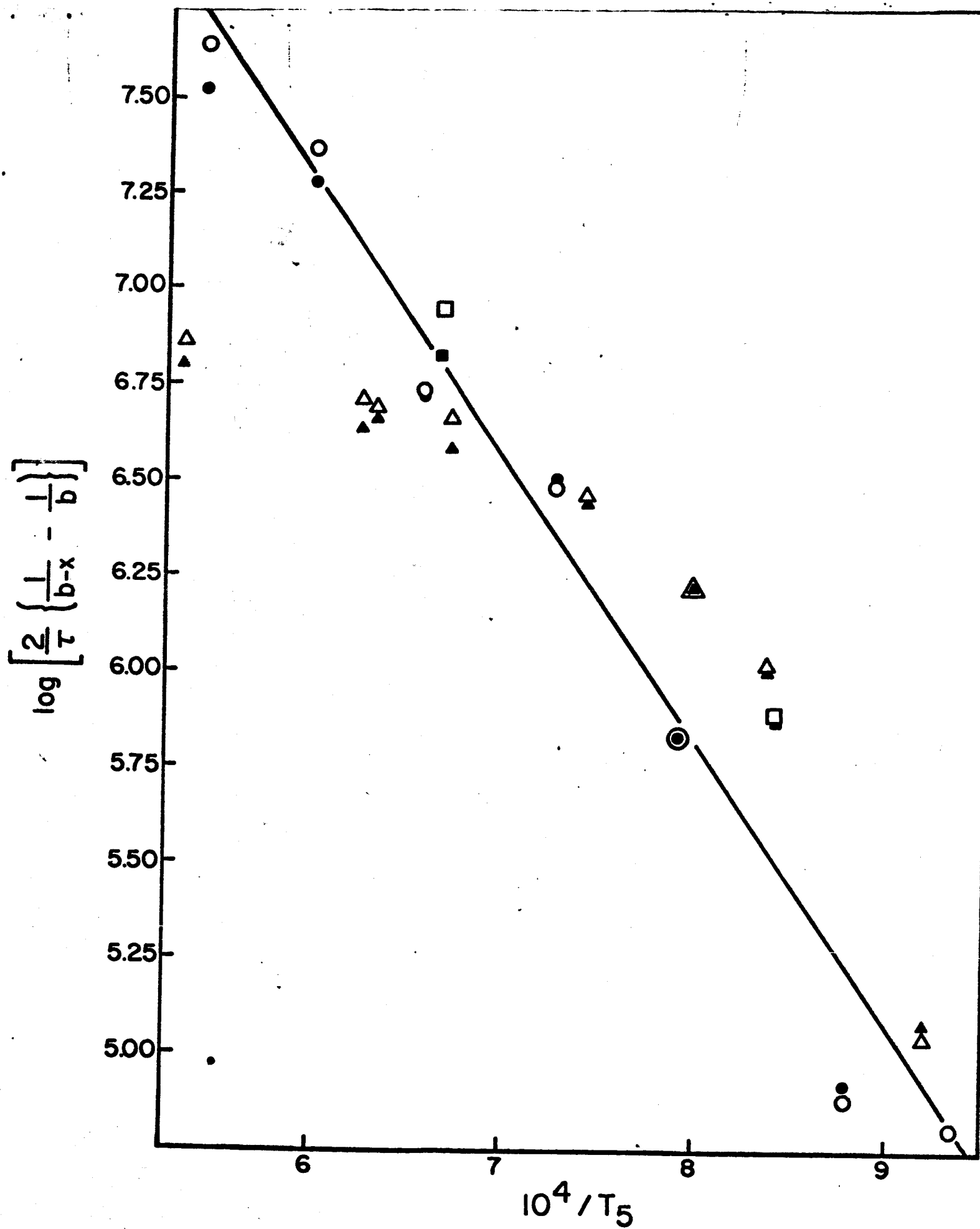
$$\frac{(HCN)}{\tau} = k_4 <H_2>^2 <C_2N_2>^{0.5} (Ar)^1$$

$$E \approx 43.1 \text{ kcal/mole.}$$

Figure 4. Justification for total order. Plot of  $\log R$  vs  $\log \rho_5$

$$R = k_4 (H_2)^x (C_2N_2)^y (Ar)^z$$

$$\text{Slope} = x + y + z = 3.58$$



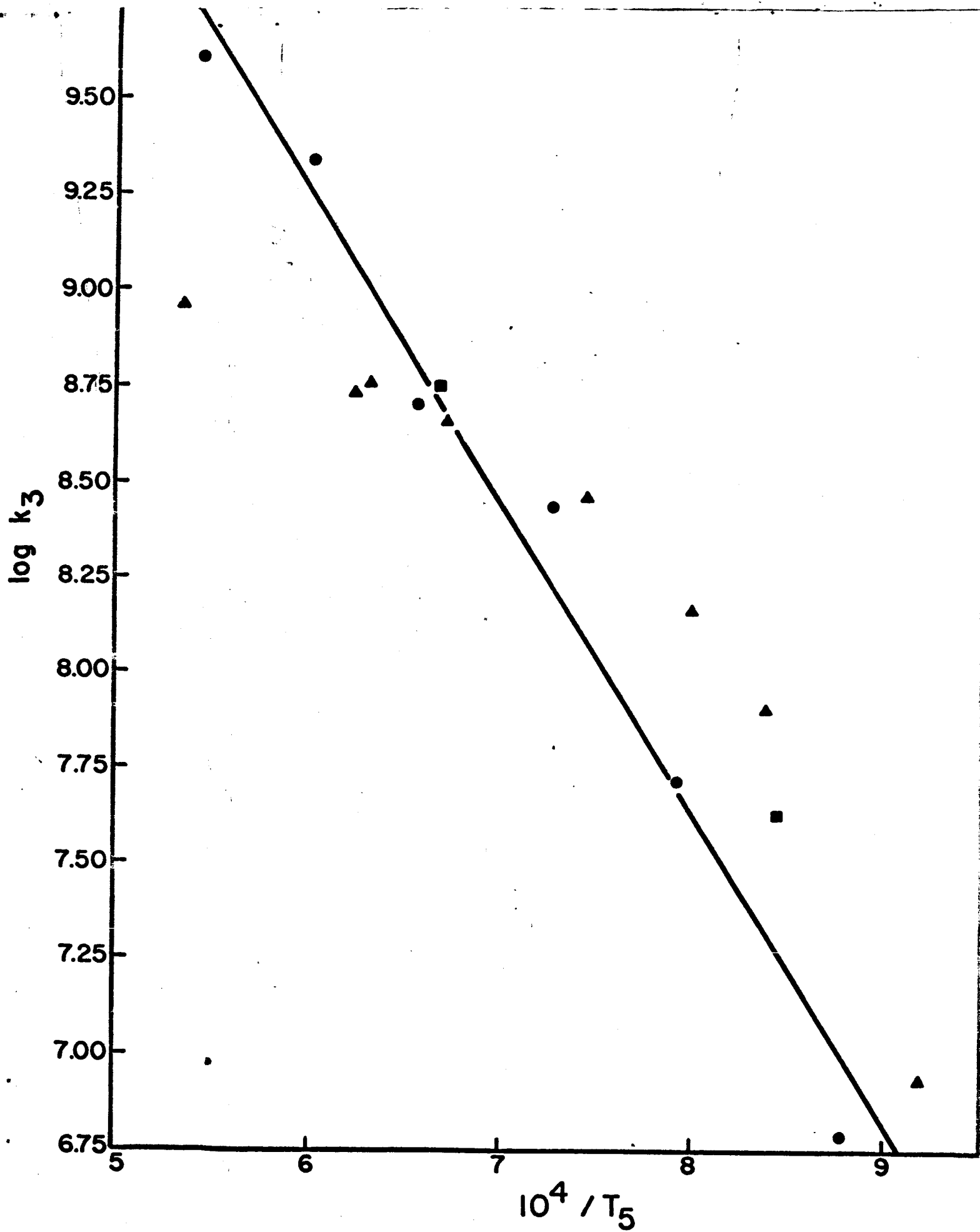


Fig. 2 ( $C_2N_2 + H_2$ )

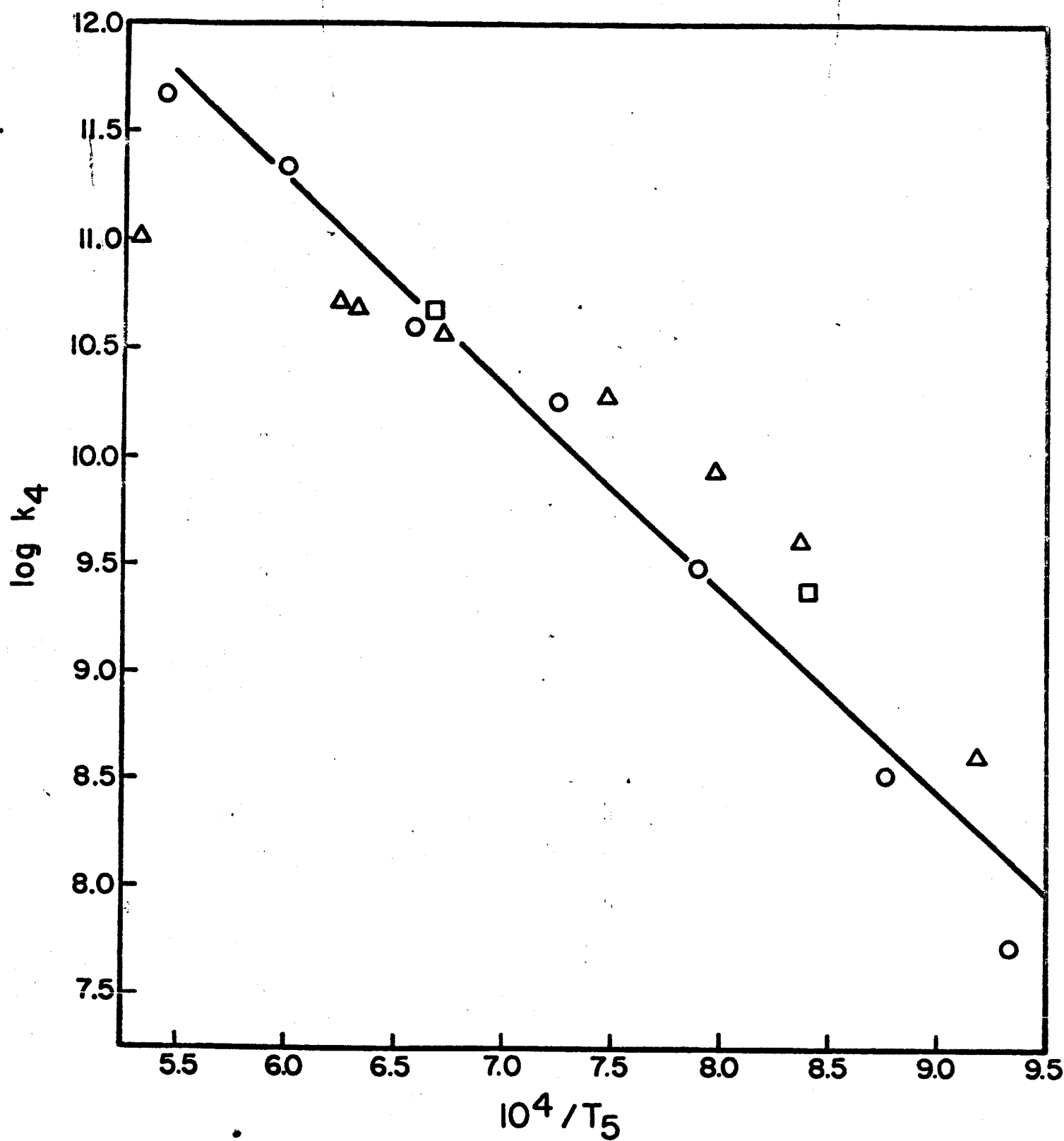


Fig. 3 ( $C_2N_2 + H_2$ )

